Abstract No. Crof0357

XAS studies of $CuIr_2S_4$

M. Croft[1,2], W. Caliebe[2], H. Woo[3], T. Tyson[3], D. Sills[1], Y. S. Hor[1], and S-W. Cheong[1]
([1]Rutgers University, [2]NSLS, [3]NJIT)

Beamline(s): X18B, X19A

At 230 K the cubic spinel compound $CuIr_2S_4$ undergoes a first order transition from a metallic (M), paramagnetic state to a low temperature distorted, diamagnetic, charge-ordered-dimerized insulating (I) state. In the absence of electronic/structural understanding of this unusual transition we have undertaken x-ray absorption spectroscopy (XAS) measurements on this system.

In Figure 1 a we show Ir-L_3 (top) and S-K (bottom) edge measurements for $CuIr_2S_4$. The Ir-L_3 white line (WL) features are due to transitions into final 5d states. With increasing electron transfer out of the 5d-odbitals, this WL feature increases in spectral weight and shifts to higher energy, as can be clearly seen by comparing the d^8-Ir-metal and d^5-IrO_2 spectra. The intensity and centrum of the $CuIr_2S_4$, Ir-L_3 edge indicates a d-hole count greater than in Ir-metal and less than in IrO_2. $CuIr_2Se_4$ appears to have a somewhat greater Ir-d DOS near E_F, relative to $CuIr_2S_4$.

The Ir-L_3 WL feature of $CuIr_2S_4$ has three components: the intense A-feature due to transitions into the 4 e_g hole final states per Ir; a weak unresolved contribution, near the A' energy range, due the ½ t_{2g} hole per Ir; and the B-feature due to Ir-S hybridization at higher energies. Notably detailed measurements of the Ir-L_3-WL feature revealed no changes across the in the M-I transition.

The S-K edge spectrum in Figure 1-bottom has an energy scale and displacement suitable for direct comparison to the Ir-L_3 edge. The S-K a- and a'- features are (aligned with the Ir A- and A' features) and respectively involve S-p/Ir-d(e_g) and S-p/Ir-d(t_{2g}) hybridized states. Thus the S-K edge provides a probe of the Ir-d states by the dipole transitions into the S-p component of the Ir-d/S-p hybrid states. Again the S-K b-feature is presumably involves the S-Ir hybridization that created the Ir-L_3 B-feature.

In Figure 2 the I- and M- phase Cu-K edge spectra of $CuIr_2S_4$ are shown along with those of a series of Cu standards. The energy and shoulder- character of the onset-feature in $CuIr_2S_4$ support a Cu^{1+} character. Only a small broadening of the fine structure features are observed in the I-phase consistent with the a distribution of differing local Cu-environments in the complex, charge-ordered, spin-dimerized I-phase.

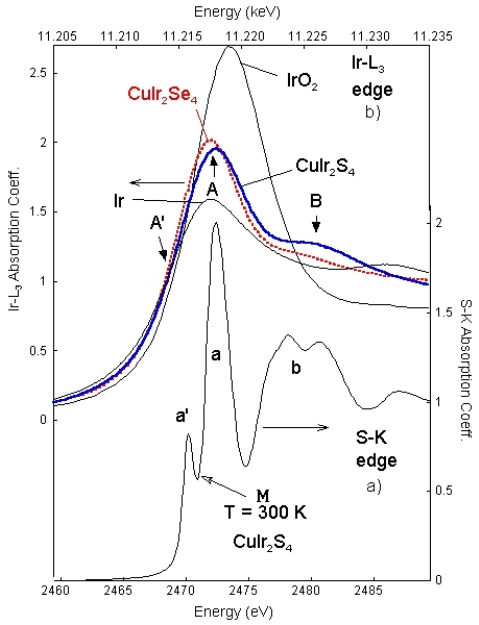

Figure1 (top) The Ir-L_3 edges of elemental Ir, IrO_2, $CuIr_2Se_4$, and $CuIr_2S_4$.
(bottom) The S-K edges of $CuIr_2S_4$. The a and a' features are associated with the S-p hybridization with Ir-d t_{2g} and e_g states respectively.

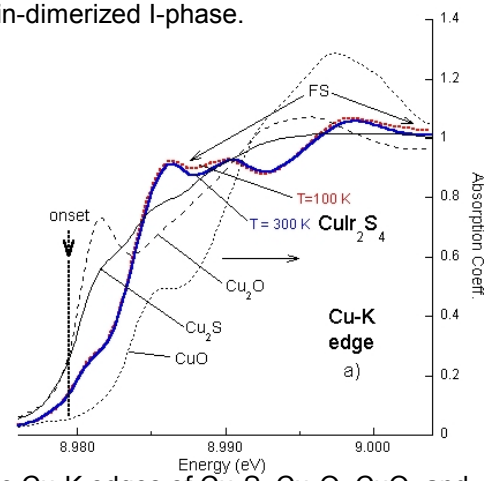

Figure 2 The Cu-K edges of Cu_2S, Cu_2O, CuO, and $CuIr_2S_4$, in the I-phase at T= 100 K and in the M-phase at 300 K. The range of the fine structure (FS) oscillations above the edge, in which the I-phase FS is broadened, is labeled.